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(54) **Polyquaternary ammonium compounds and cosmetic compositions containing them.**

(57) Novel polyquaternary ammonium compounds are prepared by polycondensation of diamino compounds and a dicarboxylic acid. The compounds are suitable for use in cosmetic compositions and as scale inhibitors and flocculants.

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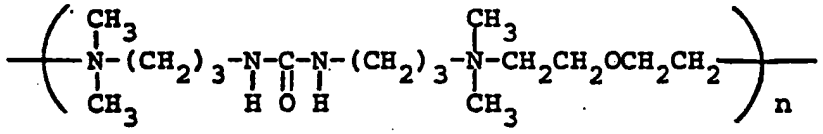
POLYQUATERNARY AMMONIUM COMPOUNDS FOR USE IN COSMETIC FORMULATIONS

BACKGROUND OF THE INVENTION

The invention relates to scale inhibitors, flocculants and conditioning agents for skin and hair, and processes for their preparation and their use. The compounds of this invention are novel polyquaternary ammonium compounds.

U.S. Patent No. 4,157,388 of Christiansen describes compositions containing polyquaternary ammonium compounds for use as hair conditioners and antistats and humectants for fibrous textile products. These compounds are generally liquid at room temperature. Mirapol® A-15 is a compound in accordance with Examples of Christiansen having the formula:



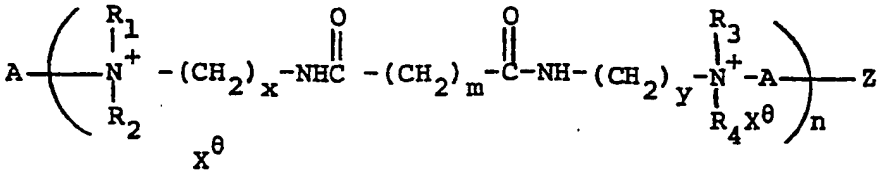
wherein n is at least one. The present polyquaternary ammonium compounds were found to be easier to work with since they do not generally require a particular order of addition and can be added in the oil or water phase. The present compounds in general also are found to have a better water solubility than the prior art compounds of Christiansen.

SUMMARY OF THE INVENTION AND DESCRIPTION OF THE PREFERRED EMBODIMENTS

The compounds of the present invention are conditioners and softeners having outstanding properties for use in hair and skin care compositions such as shampoos, soaps and lotions, and for use in scale inhibition and as

flocculants.

The present compounds are of the general Formula (I):



wherein R_1, R_2, R_3 and R_4 may be the same or different and are selected from the group consisting of hydrogen, methyl, ethyl, propyl, $-CH_2CH_2OH$, $-CH_2CH(OH)CH_3$ and $-CH_2CH_2(OCH_2CH_2)_pOH$ wherein p is an integer from 0 to 6 with the proviso that not all of R_1, R_2, R_3 and R_4 are hydrogen;

x and y are the same or different and are an integer from 1 to 6;

n is at least one, and ranges up to 100 or more;

m is an integer from 0 to 34;

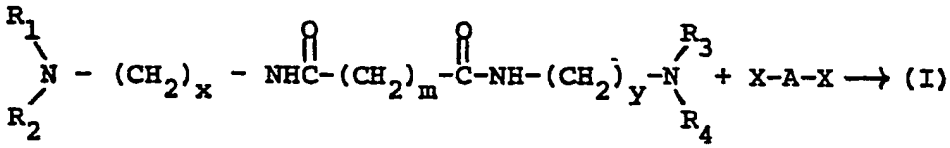
X is halogen;

Z is halogen or amino-diamido ammonium residue; and

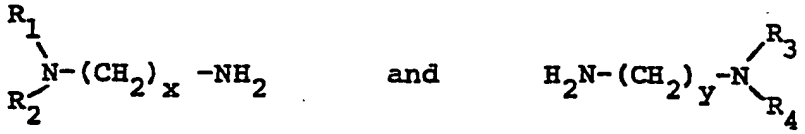
A is the residue of a dihalide.

The quaternizing agents X-A-X are organic dihalides, preferably dichlorides, such as $ClCH_2CH_2OCH_2CH_2Cl$, $ClCH_2CH_2-O-CH_2CH_2-O-CH_2CH_2Cl$, $ClCH_2CH_2Cl$, $BrCH_2CH_2Br$, $Cl(CH_2)_6Cl$, $ClCH_2CH_2CH_2Cl$ and $ClCH_2CH(OH)CH_2Cl$.

The polyquaternary compounds are prepared by condensation of a polyamine and a quaternizing agent as follows:



The polyamine in turn is prepared by condensation of two diamino compounds with a dicarboxylic acid. The diamino compounds are of the formula



and may be identical, wherein x is y and R_1 and R_2 are

identical to R_3 and R_4.

The polyquaternary ammonium compounds of the invention are generally present in amounts of from about 1 to 10% by weight based on the total cosmetic composition. Shampoos and liquid soaps generally contain about 1 to 10% by weight and lotions generally contain about 0.5 to 5% by weight.

The cosmetic formulations comprise a suitable cosmetic carrier, the composition of which carrier depends on the purpose for which the final composition is intended. Thus, different carriers will be used dependent on whether the composition is to be used as a shampoo, a soap etc. These carriers are as described in the art. They may contain surfactants such as sodium lauryl sulfate, sodium lauryl ether sulfate, sodium lauryl sarcosinate, lauroamphocarboxyglycinate or co-coamphocarboxyglycinate, solvents such as glycol and propylene glycol, proteins, citric acid, coloring agents, preservatives, fragrances, mineral oils, thickeners such as sodium chloride, PEG 6000 distearate, PEG 80 sorbitan laurate, cocamide DEA, lauramide DEA or hydroxypropyl methylcellulose, vitamins, silicones, emollients such as lanolin, isopropyl palmitate, isopropyl myristate or petrolatum and viscosity builders such as carrageenan, carbomers or cocamidopropyl hydroxy sultaine. Where appropriate, CTFA designation is provided herein above and hereinafter.

EXAMPLE I

A. To a reaction flask was charged 438 grams (3 moles) of adipic acid. After heating to about 55°C., 612 grams (6 moles) of dimethylamino-propylamine was added in about five minutes. During this addition the temperature rose to 101°C. The reaction mixture was heated to 165-170°C. in about 3 to 4 hours. Distillation started at about 147°C. After a temperature of 165°C. was reached, 62 grams of dimethylamino-propylamine (DMAPA) was added over a half hour period. The reaction mixture was then heated to 180 to 185°C. in about two hours. After a temperature of 180°C.

was reached, 62 grams of DMAPA was added in about a half hour and the temperature maintained at 180-185°C. for 1/2 hour. Vacuum was applied to remove water and excess DMAPA at a gradual increase to 5-10mm. The vacuum of 5-10mm was maintained for an hour at 180-185°C. The reaction mixture was cooled to 100°C. and vacuum decreased to recover Adipic Condensate.

The above reaction was repeated by replacing adipic acid (1) with equal molar amounts of azelaic acid and (2) with equal molar amounts of dimer acid $HOOC-(CH_2)_{34}-COOH$.

B. To a two liter reaction flask was charged 282.73 grams (0.88 moles) of Adipic Condensate formed under Example A above and 152.24 g water and the mixture was heated to 90°C. Over four hours 122.28 g (0.855 moles) dichloroethylether was added while a temperature of 90-100°C. was maintained. After the addition was completed, the reaction mass was heated to 100°C. and held for 5 hours at about 100°C. The reaction was found to be 99.7% completed by chloride ion analysis.

115.8 g Water was added to the amber colored material and the mixture heated to distill 51.4 g distillate to remove traces of unreacted dichloroethylether. The final product was a clear amber colored liquid. The pH of a 10% aqueous solution was 8.32. The solids content was 68.2% by Karl Fischer (31.8% water) determination (as described by the American Oil Chemistry Society). The compound was found to have a value for n of about 115, determined from an intrinsic viscosity average molecular weight $\bar{M}_w$ of 52,500 and an $\bar{M}_n$ (number average molecular weight) of 45,800.

EXAMPLE II

The above reaction B was repeated by replacing the Adipic Condensate by the product of Example A using azelaic acid rather than adipic acid resulting in an azelaic acid derived product of the invention for use in Conditioning Shampoo C hereafter.

EXAMPLE III

The above reaction B was repeated by replacing dichloroethylether with 1,6-dichloro-hexane.

EXAMPLE IV

Also, azelaic acid derivative was prepared by reacting azelaic condensate with 1,6-dichloro-hexane.

Application Examples

Two polyquaternaries according to the invention were evaluated as conditioners in hair and skin care products.

Four formulations were prepared having the following ingredients:

CONDITIONING SHAMPOO

	A	B	C	D
Sodium Lauryl Ether Sulfate	21.0	21.0	21.0	21.0
MIRATAINE® CB	15.0	15.0	15.0	15.0
MIRANOL® C2M CONC.	10.5	10.5	10.5	10.5
MIRAPOL® A-15	2.1	-	-	-
Product of Example IB	-	2.1	-	-
Product of Example II	-	-	2.1	-
Water	51.4	51.4	51.4	53.5

Each formulation was adjusted to a pH of 7.0.

Mirataine CB is cocamidopropyl betaine and is a high foamer and viscosity builder.

Miranol C2M Conc. is a viscous clear aqueous amphoteric surfactant solution derived from coconut fatty acids, specifically a dicarboxymethylated derivative of cocoimidazoline.

Mirapol A-15 is a hair and skin conditioner as described in U.S. Patent No. 4,157,388.

The four formulations were evaluated by testing of hair swatches as to wet comb and dry comb results, anti-static effect, softness, shine etc. Formulations B and C were found to perform better than A as regards conditioning ability, that is manageability and wet and dry comb out. C was found to be slightly better than B.

CONDITIONING SHAMPOO

	A	B	C	D
Alpha Olefin Sulfonate (A.O.S.) (40%)	15.0	15.0	15.0	15.0
MIRANOL® 2MCAS-MOD.	15.0	15.0	15.0	15.0
MIRATAINE® CBS	15.0	15.0	15.0	15.0
MIRAPOL® A-15	2.1	-	-	-
Example IB	-	2.1	-	-
Example II	-	-	2.1	-
POLYSORBATE 20 (TWEEN® 20, ICI Americas inc.)	2.0	2.0	2.0	2.0
WATER	50.9	50.9	50.9	53.0

Miranol 2MCAS-Mod. is a mixture of the lauryl sulfate and laureth - 3 sulfate salts of a dixarboxy-methylated derivative of a cocoimidazoline having one-eye irrating properties.

Mirataine CBS is cocamidopropyl hydroxysultaine.

Each formulation was adjusted to a pH of 7.0.

The same evaluation as above was performed on hair swatches and again C was found the best and B second best.

SOFT SOAP

	A	B	C	D	E
A.O.S. (40%)	15.0	15.0	15.0	15.0	15.0
CEDEPAL® TD 404M	10.0	10.0	10.0	10.0	10.0
MIRATAINE® CB	20.0	20.0	20.0	20.0	20.0
COCAMIDE DEA (SUPER AMIDE GR, Onyx Chem. Co.)	2.5	2.5	2.5	2.5	2.5
MIRAPOL® A-15	2.1	-	-	-	-
Example IB	-	2.1	-	-	-
Example II	-	-	2.1	-	-
POLYQUATERNIUM 7 MERQUAT 550 (Merck Chem. Co.)	-	-	-	2.1	-
GLYCOL STEARATE (CERASYNT, IP Van Dyk & Co.)	1.0	1.0	1.0	1.0	1.0
GLYDANT® (DMDM HYDANTOIN, Glycochemicals)	0.2	0.2	0.2	0.2	0.2

SOFT SOAP (CONT.)

	A	B	C	D	E
NaCl	1.0	1.0	1.0	1.0	1.0
WATER	48.2	48.2	48.2	48.2	50.3

The pH of each formulation was adjusted to 7.0.

Cedepal TD 404 M is sodium trideceth sulfate.

Super Amide GR is a cocodiethanolamide.

Merquat 550 is a cationic polymer.

Glydant is a preservative.

A panel of five people after washing their hands with the five formulations chose C as the best in after-feel and skin conditioning, B was the second best and slightly better than D.

SHEEN ACTIVATOR

	A	B	C	D
WATER	81.4	81.4	81.4	83.5
MIRAPOL® A-15	2.1	-	-	-
Example IB	-	2.1	-	-
Example II	-	-	2.1	-
GLYCERINE	10.0	10.0	10.0	10.0
PEPTEIN® 2000 (Hormel)	5.0	5.0	5.0	5.0
PHENOXYETHANOL (EMERESSENCE 1160, Emery Industries Inc.)	1.0	1.0	1.0	1.0
CELLOSIZE® QP 4400 (Union Carbide)	0.5	0.5	0.5	0.5

The formulations were adjusted to a pH of 5.5.

The four formulations above were evaluated as sheen activators and pre-style lotions to determine enhancement in shine and setting properties.

A panel of five people chose C as the best and B as second best.

SKIN MOISTURIZER/CONDITIONER

	A	B	C	D
Self Emulsifying Wax	7.5	7.5	7.5	7.5
PEG-400 Distearate	2.5	2.5	2.5	2.5
Stearic Acid	1.0	1.0	1.0	1.0
Cetyl Alcohol	1.0	1.0	1.0	1.0
MIRAPOL A-15	2.1	-	-	-
Example IB	-	2.1	-	-
Example II	-	-	2.1	-
MERQUAT 100	-	-	-	2.1
PROPYLENE GLYCOL	3.5	3.5	3.5	3.5
METHYL PARABEN	0.1	0.1	0.1	0.1
PROPYL PARABEN	0.2	0.2	0.2	0.2
Water	82.1	82.1	82.1	82.1

Prototype C was chosen as the best in skin Softening and Conditioning. Prototype B was second best.

The new polyquaternary ammonium compounds were evaluated as antistats in hair care products.

Eight formulations were prepared having the following ingredients:

	A	B	C	D	E	F	G	H	Control (untreated)
Sodium lauryl ether sulfate (Maprofix ES)	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	-
Mirataine CB	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	-
Miranol C2M	10.5	10.5	10.5	10.5	10.5	10.5	10.5	10.5	-
Example IV*	1.5	-	-	-	-	-	-	-	-
Example II*	-	1.5	-	-	-	-	-	-	-
Example III*	-	-	1.5	-	-	-	-	-	-
Example IB*	-	-	-	1.7	-	-	-	-	-
Mirapol A-15*	-	-	-	-	1.5	-	-	-	-
Merquat 100*	-	-	-	-	-	2.5	-	-	-
Polymer JR-400* (3% solution)	-	-	-	-	-	-	33.3	-	-

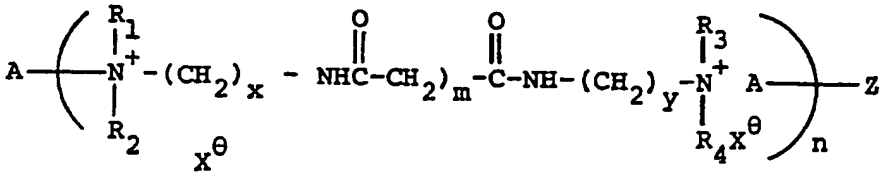
	A	B	C	D	E	F	G	H	Control (untreated)
Water	52.0	52.0	52.0	51.8	52.0	51.0	20.2	53.5	-
$X10^{-7}$ Coulombs	9.0	10.2	9.7	1.4	7.2	7.1	8.4	9.2	4.7

*Used 1% on active basis.

Hair swatches were soaked for half hour in a 25% solution of the above formulas and rinsed with 40°C. water for one minute. The hair swatches were dried overnight at ambient temperature and the antistatic property was evaluated by measuring electrostatic charges with an Electrometer (Keithley Model 610 C.). Formulation (D) exhibited the lowest static charge of the eight formulas. There was no significant difference in values obtained for the other formulations.

CLAIMS

1. A polyquaternary ammonium compound of the formula:



wherein R_1, R_2, R_3 and R_4 are the same or different and are selected from the group consisting of hydrogen, methyl, ethyl, propyl, $-CH_2CH_2OH$, $-CH_2CH(OH)CH_3$, and $-CH_2CH_2(OCH_2CH_2)_pOH$ wherein p is 0 or an integer from 1 to 6, with the proviso that not all of R_1, R_2, R_3 and R_4 are hydrogen;

x and y are the same or different and are an integer from 1 to 6;

n is at least one,

m is an integer from 0 to 34;

X is halogen;

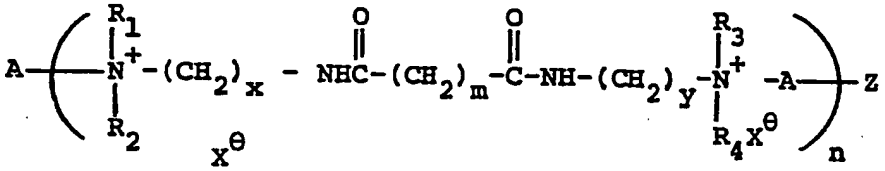
Z is halogen or amino-diamido ammonium residue; and

A is the residue of a dihalide.

2. A compound according to claim 1, wherein X is halogen and A is $-CH_2CH_2-O-CH_2CH_2-$.

3. A compound according to claim 1 or 2, wherein m is 4 and x is 3.

4. A cosmetic composition which comprises a suitable cosmetic carrier and a quaternary ammonium compound of the formula:



wherein R_1, R_2, R_3 and R_4 are the same or different and are selected from the group consisting of hydrogen, methyl, ethyl, propyl, $-CH_2CH_2OH$, $-CH_2CH(OH)CH_3$, and $-CH_2CH_2(OCH_2CH_2)_pOH$ wherein p is 0 or an integer from 1 to 6, with the proviso that not all of R_1, R_2, R_3 and R_4 are hydrogen;

x and y are the same or different and are an integer from 1 to 6;

n is at least one,

m is an integer from 0 to 34;

X is halogen;

Z is halogen or amino-diamido ammonium residue; and

A is the residue of a dihalide.

5. A composition according to claim 4, wherein X is halogen and A is $-CH_2CH_2-O-CH_2CH_2-$.

6. A composition according to claim 4 or 5, wherein m is 4 or 7 and x and y are each 3.

7. A composition according to any one of claims 4 to 6, wherein the cosmetic carrier is one for use in hair formulations.

8. A composition according to claim 7, wherein the hair formulation is a shampoo.

9. A composition according to any one of claims 4 to 6, wherein the cosmetic carrier is one for use in skin care products.

10. A composition according to claim 9, wherein the skin care product is a soap.

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European Patent Office

Application number

EP 83 11 1302

EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
X	GB-A-2 066 663 (L'OREAL) * Page 1, example 27 *	1-10	C 07 C 103/87 A 61 K 7/06 A 61 K 7/48

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

C 07 C 103/00
A 61 K 7/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23-07-1984	GAUTIER R.H.A.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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